AT 621, Fall 2012

Homework #3

Due Wednesday, September 26

Problem 1.

Estimate the rate of photolysis of NO_2 at noon on December 1 at 40° N. Do this by extending the calculation (shown in the notes) by Finlayson-Pitts and Pitts. Tables of necessary data for NO_2 are attached.

Problem 2.

Use the results from Problem 1 and the data in Table 6.1 of the text to evaluate the "typical" value of k_1/k_3 = 10 ppb (used to illustrate the PSSR on pp. 209-210 of the text). Note that a unit conversion is required; recall that you have a table in your notes of T and density as functions of altitude. (Also see Appendix of text for useful information.)

Problem 3.

Use the photolysis code on the web http://chem.atmos.colostate.edu/AT621/RadiationCode.html to compute photolysis rate constants as functions of latitude, time of year, and time of day as specified below. Comment on what you find.

a) Re-calculate the same rate constant you found in problem 1.

b) Reactions 2 and 3 as functions of time of day on July 1, in Fort Collins.

c) Reaction 30 as a function of altitude in the tropics at noon on July 1.

Problem 4.

Problem 6.1 in Jacob text (parts 1-3 only)

Problem 5.

Problem 6.2 in Jacob text

Problem 6.

Problem 6.5 in Jacob text

Figure 3.27 shows selected values of the experi- nentally determined primary quantum yields for reaction (13) as a function of wa[illegible]h in the region 295 to 445 nm. Also shown are expressions for the quan- um [illegible] dependence on wavelength given by Jones and Bayes (1973a) and rec- ommended by De More et al. (1983, 1985):

$$\phi(295 \le \lambda \le 365\ \text{nm}) = 1.0 - 0.0008\,(\lambda - 275)$$

$$\phi(295 \le \lambda \le 375\text{nm}) = 1.0 - 0.0025(\lambda - 295)$$

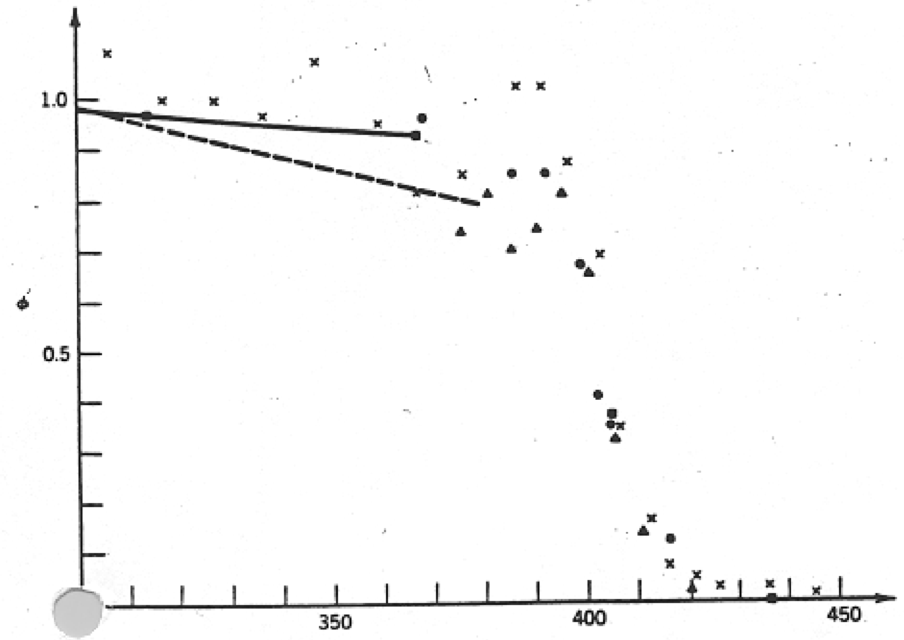

FIGURE 3.27. Selected primary quantum yields as a function of wavelength for the photolysis of NO_2. Solid line is expression recommended by De More et al. (1983, 1985), dashed line by Atkinson and Lloyd (1984). Data from: ■, Pitts et al. (1964); ×, Jones and Bayes (1973a); ●, Gaedtke and Troe (1975); ▲, Harker et al. (1977).

TABLE 3.22. Absorption Cross Sections, Base e, for NO at 298°K

λ (nm)	$10^{20}\,\sigma$ (cm^2 molecule^{-1})	λ (nm)	$10^{20}\,\sigma$ (cm^2 molecule
185	26.0	300	11.7
190	29.3	305	16.6
195	24.2	310	17.6
200	25.0	315	22.5
205	37.5	320	25.4
210	38.5	325	27.9
215	40.2	330	29.9
220	39.6	335	34.5
225	32.4	340	38.8
230	24.3	345	40.7
235	14.8	350	41.0
240	6.70	355	51.3
245	4.35	360	45.1
250	2.83	365	57.8
255	1.45	370	54.2
260	1.90	375	53.5
265	2.05	380	59.9
270	3.13	385	59.4
275	4.02	390	60.0
280	5.54	395	58.9
285	6.99	400	67.6
290	8.18	405	63.2
295	9.67	410	57.7

Source: De More et al., 1983; data from Bass et al., 1976.

TABLE 3.25. Primary Quantum Yields, ϕ, for NO_2 Photolysis into NO + $O(^3P)$

λ (nm)	ϕ	λ (nm)	ϕ	λ (nm)	ϕ
375	0.77	389	0.78	400	0.68
376	0.78	390	0.80	401	0.65
377	0.92	391	0.88	402	0.62
378	0.82	392	0.84	403	0.57
379	0.87	393	0.90	404	0.42
380	0.90	394	0.90	405	0.32
381	0.81	394.5	0.86	406	0.33
382	0.70	395	0.84	407	0.25
[illegible]	0.68	395.5	0.81	408	0.20
[illegible]	0.70	396	0.83	409	0.19
[illegible]	0.77	396.5	0.88	410	0.15
386	0.84	397	0.82	411	0.10
387	0.75	398	0.77	415	0.067
388	0.81	399	0.78	420	0.023

Source: De More et al., 1985; data based on product ($\phi\sigma$) of Harker et al., (1977) and values of σ of Bass et al. (1976).